

[00266] In another embodiment the polymer produced by this invention may be blended with elastomers (preferred elastomers include all natural and synthetic rubbers, including those defined in ASTM D1566). In a preferred embodiment elastomers are blended with the polymer produced by this invention to form rubber toughened compositions. In a particularly preferred embodiment the rubber toughened composition is a two (or more) phase system where the rubber is a discontinuous phase and the polymer is a continuous phase. Examples of preferred elastomers include one or more of the following: ethylene propylene rubber, ethylene propylene diene monomer rubber, neoprene rubber, styrenic block copolymer rubbers (including SI, SIS, SB, SBS, SIBS and the like), butyl rubber, halobutyl rubber, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene. This blend may be combined with the tackifiers and/or other additives as described above.

[00267] In another embodiment the polymer produced by this invention may be blended with impact copolymers. Impact copolymers are defined to be a blend of isotactic PP and an elastomer such as an ethylene-propylene rubber. In a preferred embodiment the blend is a two (or more) phase system where the impact copolymer is a discontinuous phase and the polymer is a continuous phase.

[00268] In another embodiment the polymer produced by this invention may be blended with ester polymers. In a preferred embodiment the blend is a two (or more) phase system where the polyester is a discontinuous phase and the polymer is a continuous phase.

[00269] In a preferred embodiment the polymers of the invention described above are combined with metallocene polyethylenes (mPE's) or metallocene polypropylenes (mPP's). The mPE and mPP homopolymers or copolymers are typically produced using mono- or bis-cyclopentadienyl transition metal catalysts in combination with an activator of alumoxane and/or a non-coordinating anion in

solution, slurry, high pressure or gas phase. The catalyst and activator may be supported or unsupported and the cyclopentadienyl rings by may substituted or unsubstituted. Several commercial products produced with such catalyst/activator combinations are commercially available from ExxonMobil Chemical Company in Baytown, Texas. under the tradenames EXCEED™, ACHIEVE™ and EXACT™. For more information on the methods and catalysts/activators to produce such mPE homopolymers and copolymers see WO 94/26816; WO 94/03506; EPA 277,003; EPA 277,004; U.S. Pat. No. 5,153,157; U.S. Pat. No. 5,198,401; U.S. Pat. No. 5,240,894; U.S. Pat. No. 5,017,714; CA 1,268,753; U.S. Pat. No. 5,324,800; EPA 129,368; U.S. Pat. No. 5,264,405; EPA 520,732; WO 92 00333; U.S. Pat. No. 5,096,867; U.S. Pat. No. 5,507,475; EPA 426 637; EPA 573 403; EPA 520 732; EPA 495 375; EPA 500 944; EPA 570 982; WO91/09882; WO94/03506 and U.S. Pat. No. 5,055,438.

[00270] In another embodiment the olefin polymer of this invention, preferably the polypropylene homopolymer or copolymer of this invention, can be blended with another homopolymer and/or copolymer, including but not limited to, homopolypropylene, propylene copolymerized with up to 50 weight % of ethylene or a C4 to C20 alpha-olefin, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene and/or butene and/or hexene, polybutene, ethylene vinyl acetate, low density polyethylene (density 0.915 to less than 0.935 g/cm³) linear low density polyethylene, ultra low density polyethylene (density 0.86 to less than 0.90 g/cm³), very low density polyethylene (density 0.90 to less than 0.915 g/cm³), medium density polyethylene (density 0.935 to less than 0.945 g/cm³), high density polyethylene (density 0.945 to 0.98 g/cm³), ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, elastomers such as ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block

copolymer elastomers such as SBS, nylons (polyamides), polycarbonates, PET resins, crosslinked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, high molecular weight polyethylene having a density of 0.94 to 0.98 g/cm³ low molecular weight polyethylene having a density of 0.94 to 0.98 g/cm³, graft copolymers generally, polyacrylonitrile homopolymer or copolymers, thermoplastic polyamides, polyacetal, polyvinylidene fluoride and other fluorinated elastomers, polyethylene glycols and polyisobutylene.

[00271] In a preferred embodiment the olefin polymer of this invention, preferably the polypropylene polymer of this invention, is present in the blend at from 10 to 99 weight %, based upon the weight of the polymers in the blend, preferably 20 to 95 weight %, even more preferably at least 30 to 90 weight %, even more preferably at least 40 to 90 weight %, even more preferably at least 50 to 90 weight %, even more preferably at least 60 to 90 weight %, even more preferably at least 70 to 90 weight %.

[00272] The blends described above may be produced by mixing the two or more polymers together, by connecting reactors together in series to make reactor blends or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers can be mixed together prior to being put into the extruder or may be mixed in an extruder.

Any of the above polymers, including the polymers produced by this invention, may be functionalized. Preferred functional groups include maleic acid and maleic anhydride. By functionalized is meant that the polymer has been contacted with an unsaturated acid or anhydride. Preferred unsaturated acids or anhydrides include any unsaturated organic compound containing at least one double bond and at least one carbonyl group. Representative acids include carboxylic acids, anhydrides, esters and their salts, both metallic and non-metallic. Preferably the

organic compound contains an ethylenic unsaturation conjugated with a carbonyl group ($-C=O$). Examples include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, alpha.methyl crotonic, and cinnamic acids as well as their anhydrides, esters and salt derivatives. Maleic anhydride is particularly preferred. The unsaturated acid or anhydride is preferably present at about 0.1 weight % to about 10 weight %, preferably at about 0.5 weight % to about 7 weight %, even more preferably at about 1 to about 4 weight %, based upon the weight of the hydrocarbon resin and the unsaturated acid or anhydride.

[00273] In a preferred embodiment the unsaturated acid or anhydride comprises a carboxylic acid or a derivative thereof selected from the group consisting of unsaturated carboxylic acids, unsaturated carboxylic acid derivatives selected from esters, imides, amides, anhydrides and cyclic acid anhydrides or mixtures thereof.

Applications

For purposes of this invention and the claims thereto, the following tests are used, unless otherwise indicated.

Tensile strength, Tensile strength at break and elongation at break are measured by ASTM D 1708. Elongation at break is also called strain at break or percent elongation.

Peel strength -ASTM D-1876 (also referred to as Peel adhesion at 180 ° peel angle, 180° peel strength, 180 ° peel adhesion, T-Peel strength, T-Peel.)

Dynamic Storage modulus also called storage modulus is G' .

Creep resistance ASTM D-2293

Rolling Ball Tack PSTC 6

Hot Shear Strength is determined by suspending a 1000 gram weight from a 25mm wide strip of MYLAR polyester film coated with the polymer or adhesive

formulation which is adhered to a stainless steel plate with a contact area of 12.5mm x 25mm. The sample is placed in a ventilated oven at 40°C. time is recorded until stress failure occurs.

Probe tack (also called Polyken probe tack) ASTM D 2979

Holding Power - PSTC 7 , also called Shear adhesion or Shear strength?.

Density - ASTM D792 at 25 °C.

Gardner color ASTM D 1544-68.

SAFT is also called heat resistance.

Tensile Strength Modulus at 100 % elongation and Young's Modulus are determined according to ASTM E-1876.

Luminence is the reflectance "Y" in the CIE color coordinates as determined by ASTM D 1925 divided by 100.

[00274] The polymer product of this invention or formulations thereof may then be applied directly to a substrate or may be sprayed thereon, typically the polymer is molten. Spraying is defined to include atomizing, such as producing an even dot pattern, spiral spraying such as Nordson Controlled Fiberization or oscillating a stretched filament like is done in the ITW Dynafiber/Omega heads or Summit technology from Nordson, as well as melt blown techniques. Melt blown techniques are defined to include the methods described in U.S. patent 5,145,689 or any process where air streams are used to break up filaments of the extrudate and then used to deposit the broken filaments on a substrate. In general, melt blown techniques are processes that use air to spin hot melt adhesive fibers and convey them onto a substrate for bonding. Fibers sizes can easily be controlled from 20-200 microns by changing the melt to air ratio. Few, preferably no, stray fibers are generated due to the inherent stability of adhesive melt blown applicators. Under UV light the bonding appears as a regular, smooth, stretched dot pattern. Atomization is a process that uses air to atomize hot melt adhesive into very small dots and convey them onto a substrate for bonding.

Lamination melt coating

[00275] The adhesives of this invention can be used in any adhesive application, including but not limited to, disposables, packaging, laminates, pressure sensitive adhesives, tapes labels, wood binding, paper binding, non-wovens, road marking, reflective coatings, and the like.

[00276] In a preferred embodiment the adhesives of this invention can be used for disposable diaper and napkin chassis construction, elastic attachment in disposable goods converting, packaging, labeling, bookbinding, woodworking, and other assembly applications. Particularly preferred applications include: baby diaper leg elastic, diaper frontal tape, diaper standing leg cuff, diaper chassis construction, diaper core stabilization, diaper liquid transfer layer, diaper outer cover lamination, diaper elastic cuff lamination, feminine napkin core stabilization, feminine napkin adhesive strip, industrial filtration bonding, industrial filter material lamination, filter mask lamination, surgical gown lamination, surgical drape lamination, and perishable products packaging.

[00277] The adhesives described above may be applied to any substrate. Preferred substrates include wood, paper, cardboard, plastic, thermoplastic, rubber, metal, metal foil (such as aluminum foil and tin foil), metallized surfaces, cloth, non-wovens (particularly polypropylene spun bonded fibers or non-wovens), spunbonded fibers, cardboard, stone, plaster, glass (including silicon oxide (SiO_x) coatings applied by evaporating silicon oxide onto a film surface), foam, rock, ceramics, films, polymer foams (such as polyurethane foam), substrates coated with inks, dyes, pigments, PVDC and the like or combinations thereof.

[00278] Additional preferred substrates include polyethylene, polypropylene, polyacrylates, acrylics, polyethylene terephthalate, or any of the polymers listed above as suitable for blends.

[00279] Any of the above substrates, and/or the polymers of this invention, may be corona discharge treated, flame treated, electron beam irradiated, gamma irradiated, microwaved, or silanized.

[00280] The adhesives produced herein, when coated in some fashion between two adherends, preferably perform such that the materials are held together in a sufficient fashion compared to a standard specification or a standard adhesive similarly constructed.

[00281] The polymer product of this invention may be used in any adhesive application described in WO 97/33921 in combination with the polymers described therein or in place of the polymers described therein.

[00282] The polymer product of this invention, alone or in combination with other polymers and or additives, may also be used to form hook and loop fasteners as described in WO 02/35956.

Characterization and Tests

[00283] Molecular weights (number average molecular weight (M_n), weight average molecular weight (M_w), and z-average molecular weight (M_z)) are determined using a Waters 150 Size Exclusion Chromatograph (SEC) equipped with a differential refractive index detector (DRI), an online low angle light scattering (LALLS) detector and a viscometer (VIS). The details of the detector calibrations have been described elsewhere [Reference: T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, 6812-6820, (2001)]; attached below are brief descriptions of the components.

[00284] The SEC with three Polymer Laboratories PLgel 10mm Mixed-B columns, a nominal flow rate $0.5 \text{ cm}^3 / \text{min}$, and a nominal injection volume 300 *microliters* is common to both detector configurations. The various transfer lines, columns and differential refractometer (the DRI detector, used mainly to determine eluting solution concentrations) are contained in an oven maintained at 135°C .

[00285] The LALLS detector is the model 2040 dual-angle light scattering photometer (Precision Detector Inc.). Its flow cell, located in the SEC oven, uses a 690 nm diode laser light source and collects scattered light at two angles, 15° and 90° . Only the 15° output was used in these experiments. Its signal is sent to a data acquisition board (National Instruments) that accumulates readings at a rate of 16 per second. The lowest four readings are averaged, and then a proportional signal is sent to the SEC-LALLS-VIS computer. The LALLS detector is placed after the SEC columns, but before the viscometer.

[00286] The viscometer is a high temperature Model 150R (Viscotek Corporation). It consists of four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity for the solution flowing through the viscometer is calculated from their outputs. The viscometer is inside the SEC oven, positioned after the LALLS detector but before the DRI detector.

[00287] Solvent for the SEC experiment was prepared by adding 6 grams of butylated hydroxy toluene (BHT) as an antioxidant to a 4 liter bottle of 1,2,4 Trichlorobenzene (TCB)(Aldrich Reagent grade) and waiting for the BHT to solubilize. The TCB mixture was then filtered through a 0.7 micron glass pre-

filter and subsequently through a 0.1 micron Teflon filter. There was an additional online 0.7 micron glass pre-filter/0.22 micron Teflon filter assembly between the high pressure pump and SEC columns. The TCB was then degassed with an online degasser (Phenomenex, Model DG-4000) before entering the SEC.

[00288] Polymer solutions were prepared by placing dry polymer in a glass container, adding the desired amount of TCB, then heating the mixture at 160 °C with continuous agitation for about 2 hours. All quantities were measured gravimetrically. The TCB densities used to express the polymer concentration in mass/volume units are 1.463 g/ml at room temperature and 1.324 g/ml at 135 °C. The injection concentration ranged from 1.0 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples.

[00289] Prior to running each sample the DRI detector and the injector were purged. Flow rate in the apparatus was then increased to 0.5 ml/minute, and the DRI was allowed to stabilize for 8-9 hours before injecting the first sample. The argon ion laser was turned on 1 to 1.5 hours before running samples by running the laser in idle mode for 20-30 minutes and then switching to full power in light regulation mode.

[00290] The branching index was measured using SEC with an on-line viscometer (SEC-VIS) and are reported as g' at each molecular weight in the SEC trace. The branching index g' is defined as:

$$g' = \frac{\eta_b}{\eta_l}$$

where η_b is the intrinsic viscosity of the branched polymer and η_l is the intrinsic viscosity of a linear polymer of the same viscosity-averaged molecular weight (M_v) as the branched polymer. $\eta_l = KM_v^\alpha$, K and α are measured values for linear polymers and should be obtained on the same SEC-DRI-LS-VIS instrument as the one used for branching index measurement. For polypropylene samples presented in this invention, K=0.0002288 and $\alpha=0.705$ were used. The SEC-DRI-LS-VIS

method obviates the need to correct for polydispersities, since the intrinsic viscosity and the molecular weight are measured at individual elution volumes, which arguably contain narrowly dispersed polymer. Linear polymers selected as standards for comparison should be of the same viscosity average molecular weight and comonomer content. Linear character for polymer containing C2 to C10 monomers is confirmed by Carbon-13 NMR the method of Randall (Rev. Macromol. Chem. Phys., C29 (2&3), p. 285-297).

[00291] Linear character for C11 and above monomers is confirmed by GPC analysis using a MALLS detector. For example, for a copolymer of propylene, the NMR should not indicate branching greater than that of the comonomer (i.e. if the comonomer is butene, branches of greater than two carbons should not be present). For a homopolymer of propylene, the GPC should not show branches of more than one carbon atom. When a linear standard is desired for a polymer where the comonomer is C9 or more, one can refer to T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, 6812-6820, (2001) for protocols on determining standards for those polymers.. In the case of syndiotactic polymers, the standard should have a comparable amount of syndiotacticity as measured by Carbon 13 NMR.

[00292] In another embodiment the polymer produced by this invention has a molecular weight distribution (M_w/M_n) of at least 2, preferably at least 5, preferably at least 10, even more preferably at least 20.

[00293] In another embodiment the polymer produced may have a unimodal, bimodal, or multimodal molecular weight distribution (M_w/M_n) distribution of polymer species as determined by Size Exclusion Chromatography (SEC). By bimodal or multimodal is meant that the SEC trace has more than one peak or inflection points. An inflection point is that point where the second

derivative of the curve changes in sign (e.g., from negative to positive or vice versus).

[00294] Peak melting point (T_m), peak crystallization temperature (T_c), heat of fusion and crystallinity were determined using the following procedure according to ASTM E 794-85. Differential scanning calorimetric (DSC) data was obtained using a TA Instruments model 2920 machine. Samples weighing approximately 7-10 mg were sealed in aluminum sample pans. The DSC data was recorded by first cooling the sample to $-50\text{ }^{\circ}\text{C}$ and then gradually heating it to $200\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{minute}$. The sample is kept at $200\text{ }^{\circ}\text{C}$ for 5 minutes before a second cooling-heating cycle is applied. Both the first and second cycle thermal events are recorded. Areas under the curves were measured and used to determine the heat of fusion and the degree of crystallinity. The percent crystallinity is calculated using the formula, $[\text{area under the curve (Joules/gram)} / B \text{ (Joules/gram)}] * 100$, where B is the heat of fusion for the homopolymer of the major monomer component. These values for B are to be obtained from the Polymer Handbook, Fourth Edition, published by John Wiley and Sons, New York 1999. A value of 189 J/g (B) was used as the heat of fusion for 100% crystalline polypropylene. For polymers displaying multiple melting or crystallization peaks, the highest melting peak was taken as peak melting point, and the highest crystallization peak was taken as peak crystallization temperature.

[00295] The glass transition temperature (T_g) was measured by ASTM E 1356 using a TA Instrument model 2920 machine.

[00296] Polymer samples for ^{13}C NMR spectroscopy were dissolved in d_2 -1,1,2,2-tetrachloroethane and the samples were recorded at 125°C . using a NMR spectrometer of 75 or 100 MHz. Polymer resonance peaks are referenced to $\text{mmmm}=21.8\text{ ppm}$. Calculations involved in the characterization of polymers by NMR follow the work of F. A. Bovey in "Polymer Conformation and

Configuration" Academic Press, New York 1969 and J. Randall in "Polymer Sequence Determination, Carbon-13 NMR Method", Academic Press, New York, 1977. The percent of methylene sequences of two in length, $\%(\text{CH}_2)_2$, were calculated as follows: the integral of the methyl carbons between 14-18 ppm (which are equivalent in concentration to the number of methylenes in sequences of two in length) divided by the sum of the integral of the methylene sequences of one in length between 45-49 ppm and the integral of the methyl carbons between 14-18 ppm, times 100. This is a minimum calculation for the amount of methylene groups contained in a sequence of two or more since methylene sequences of greater than two have been excluded. Assignments were based on H. N. Cheng and J. A. Ewen, Makromol. Chem. 1989, 190, 1931.

[00297] Ethylene content of a polymer can be measured as follows. A thin homogeneous film is pressed at a temperature of about 150°C or greater, then mounted on a Perkin Elmer PE 1760 infrared spectrophotometer. A full spectrum of the sample from 600 cm^{-1} to 4000 cm^{-1} is recorded and the monomer weight percent of ethylene can be calculated according to the following equation: Ethylene wt % = $82.585 - 111.987X + 30.045 X^2$, wherein X is the ratio of the peak height at 1155 cm^{-1} and peak height at either 722 cm^{-1} or 732 cm^{-1} , whichever is higher. The concentrations of other monomers in the polymer can also be measured using this method.

Adhesive Testing

[00298] SAFT (modified D4498) measures the ability of a bond to withstand an elevated temperature rising at 10 °F (5.5 °C) /15 min., under a constant force that pulls the bond in the shear mode. Bonds were formed in the manner described above (1 inch by 3 inch (2.5 cm x 7.6 cm) (on Kraft paper). The test specimens were suspended vertically in an oven at room temperature with a 500 gram load attached to the bottom. The temperatures at which the weight fell was recorded (when the occasional sample reached temperatures above the oven

capacity >265°F (129°C) it was terminated and averaged in with the other samples at termination temperature).

[00299] Set time is defined as the time it takes for a compressed adhesive substrate construct to fasten together enough to give substrate fiber tear when pulled apart, and thus the bond is sufficiently strong to remove the compression. The bond will likely still strengthen upon further cooling, however, it no longer requires compression. These set times were measured by placing a molten dot of adhesive on to a file folder substrate taped to a flat table. A file folder tab (1 inch by 3 inch (2.5 cm x 7.6 cm) was placed upon the dot 3 seconds later and compressed with a 500 gram weight. The weight was allowed to sit for about 0.5 to about 10 seconds. The construct thus formed was pulled apart to check for a bonding level good enough to produce substrate fiber tear. The set time was recorded as the minimum time required for this good bonding to occur. Standards were used to calibrate the process.

[00300] Once a construct has been produced it can be subjected to various insults in order to assess the effectiveness of the bond. Once a bond fails to a paper substrate a simple way to quantify the effectiveness is to estimate the area of the adhesive dot that retained paper fibers as the construct failed along the bond line. This estimate is called percent substrate fiber tear. An example of good fiber, after conditioning a sample for 15 hours at -12 °C and attempting to destroy the bond, would be an estimate of 80-100% substrate fiber tear. It is likely that 0% substrate fiber tear under those conditions would signal a loss of adhesion.

[00301] Shore A hardness was measured according to ASTM 2240. An air cooled dot of adhesive was subjected to the needle and the deflection was recorded from the scale.

[00302] Dot T-Peel was determined according to ASTM D 1876, except that the specimen was produced by combining two 1 inch by 3 inch (2.54 cm x 7.62 cm) substrate cut outs with a dot of adhesive with a volume that, when compressed under a 500 gram weight occupied about 1 square inch of area (1 inch = 2.54 cm). Once made all the specimens were pulled apart in side by side testing (at a rate of 2 inches per minute) by a machine that records the destructive force of the insult being applied. The maximum force achieved for each sample tested was recorded and averaged, thus producing the Average Maximum Force which is reported as the Dot T-Peel.

[00303] Adhesive Melt Viscosity (ASTM D-3236): Melt viscosity profiles are typically measured at temperatures from 120 °C to 190 °C using a Brookfield Thermosel viscometer and a number 27 spindle.

[00304] Peel Strength (modified ASTM D1876): Substrates (1 x 3 inches (25 x 76 mm)) are heat sealed with adhesive film (5 mils (130 μ m) thickness) at 135 °C for 1 to 2 seconds and 40 psi (0.28 MPa) pressure. Bond specimens were peeled back in a tensile tester at a constant crosshead speed of 2 in/min (51 mm/min). The average force required to peel the bond (5 specimens) apart is recorded.

[00305] Shear Adhesion Fail Temperature (SAFT) (modified ASTM D4498) measures the ability of the bond to withstand an elevated temperature rising at 10 °F (5.5°C)/15 min, under a constant force that pulls the bond in the shear mode. Bonds 1 inch by 1 inch (Kraft paper) (25 mm x 25 mm) were formed of adhesive by heat sealing as in procedure "(b)" above for 1.5 s. The test specimens were suspended vertically in an oven at 32 °C with a 500 g load attached to the bottom. The temperature at which the weight falls is recorded. Adhesives possessing high failure temperature are essential for the assembly of

packaging goods that are often subjected to very high temperatures during storage and shipping.

[00306] Peel Adhesion Failure Temperature (PAFT) was determined using following procedure modified according to the procedure of TAPPI T814 PM-77. Two sheets of 6"× 12" Kraft paper were laminated together with a one inch strip of molten adhesive heated to 177 °C. The laminated sheet was trimmed and cut into 1-inch wide strips. These strips were placed in an oven with a 100-gram of weight hanging in a peel mode. The oven temperature increased at a rate of 30 °C per hour. The sample were hung from a switch that trips when the samples fail to record the temperature of failure.

[00307] Low Temperature Substrate Fiber Tear: Kraft paper bonds are prepared as in procedure "(b)" above. The bond specimens are placed in a freezer or refrigerator to obtain the desired test temperature. The bonds are separated by hand and a determination made as to the type of failure observed. The amount of substrate fiber tear is expressed in percentage. "SF" indicates substrate failure.

[00308] Cloud point is determined by heating the adhesive blends to 121°C. and applying a small bead (approximately 1 gram) of the molten adhesive to the bulb of an ASTM thermometer. The temperature at which the molten adhesive clouds over is then noted. These measures of cloud point provide an indication of a hot melt's overall compatibility, i.e., the compatibility of the individual ingredients with each other.

[00309] Compression Molding: Plaques suitable for physical property testing were compression molded on a Carver hydraulic press. 6.5g of polymer was molded between brass plates (0.05" thick) lined with Teflon™ coated aluminum foil. A 0.033" thick chase with a square opening 4" x 4" was used to control sample thickness. After one minute of preheat at 170 ° or 180 °C, under

minimal pressure, the hydraulic load was gradually increased to ~10,000 - 15,000 lbs., at which it was held for three minutes. Subsequently the sample and molding plates were cooled for three minutes under ~10,000 to 15,000 lbs. load between the water cooled platens of the press. Plaques were allowed to equilibrate at room temperature for a minimum of two days prior to physical property testing.

[00310] Unidirectional Tensile Testing: Dogbones for tensile testing were cut from compression molded plaques using a mallet handle die. Specimen dimensions were those specified in ASTM D 1708. Tensile properties were measured on an Instron™ model 4502 equipped with a 22.48 lb. load cell and pneumatic jaws fitted with serrated grip faces. Deformation was performed at a constant crosshead speed of 5.0 in/min with a data sampling rate of 25 points/second. Jaw separation prior to testing was 0.876", from which strains were calculated assuming affine deformation. Initial modulus, stress and strain at yield (where evident), peak stress, tensile strength at break, and strain at break were calculated. A minimum of five specimens from each plaque was tested, the results being reported as the average value. All stresses quoted were calculated based upon the original cross-sectional area of the specimen, taking no account of reduced cross-section as a function of increasing strain.

[00311] The rheological properties (G' , G'') were determined on ARES instrument manufactured by Rheometric Scientific, Piscataway, New Jersey. The polymers were first melted and then cooled down at 1 °C/min. Dynamic moduli were recorded during the cooling, starting from a temperature higher than the melting point of the material by at least 30 °C down to about 80 °C. The output of the test is therefore the evolution of the storage modulus G' , the loss modulus G'' , as well as the ratio $\tan\delta = G''/G'$ as a function of temperature. Measurements were made at a constant frequency of 10 rad/s and 20 percent of strain, using a 12.5 mm diameter plate-and-plate geometry.

EXAMPLES

General

[00312] All polymerizations were performed in a liquid filled, single-stage continuous reactor using mixed metallocene catalyst systems. The reactor was a 0.5-liter stainless steel autoclave reactor and was equipped with a stirrer, a water cooling/steam heating element with a temperature controller, and a pressure controller. Solvents, propylene, and comonomers (such as butene and hexene), if present, were first purified by passing through a three-column purification system. The purification system consists of an Oxiclear column (Model # RGP-R1-500 from Labclear) followed by a 5A and a 3A molecular sieve columns. Purification columns were regenerated periodically whenever there is evidence of lower activity of polymerization. Both the 3A and 5A molecular sieve columns were regenerated in-house under nitrogen at a set temperature of 260°C and 315°C, respectively. The molecular sieve material was purchased from Aldrich. Oxiclear column was regenerated in the original manufacture. Purified ethylene from in-house supply was fed into the manifold then the reactor through a Brookfield mass flow controller. The ethylene was delivered as a gas solubilized in the chilled solvent/monomer mixture. The purified solvents and monomers were then chilled to about -15 °C by passing through a chiller before fed into the reactor through a manifold. Solvent and monomers were mixed in the manifold and fed into reactor through a single tube. All liquid flow rates are measured using Brooksfield mass flow meters or Micro-Motion Coriolis-type flow meters.

[00313] Unless otherwise noted the catalysts compounds were obtained from Albemarle.

[00314] The catalyst compounds used to produce semi-crystalline polypropylene were rac-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride, rac-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dimethyl, rac-dimethylsilylbis(2-methylindenyl)zirconium dimethyl, rac-

dimethylsilylbis(indenyl)hafnium dimethyl, and rac-1,2-ethylene-bis(4,7-dimethylindenyl)hafnium dimethyl (obtained from Boulder Scientific Company).

[00315] The catalyst compounds used to produce amorphous polypropylene were dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl, dimethylsilyl(*tert*-butylamido)(tetramethylcyclopentadienyl) titanium dimethyl (obtained from Boulder Scientific Company), [di(*p*-triethylsilylphenyl)methylene](cyclopentadienyl)(3,8-di-*t*-butylfluorenyl)hafnium dimethyl (produced according to the examples in US 6,528,670) and dimethylsilyl(tetramethylcyclopentadienyl)(N-1-adamantyl)titanium dimethyl (produced according to the examples in US Patent 5,955,625).

[00316] Dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dichloride was made according to the examples in US patent 5,057,475. The dimethyl version was obtained by dimethylation of the dichloride version.

[00317] Rac-Dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride and dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dichloride were activated with MAO (methylalumoxane). Rac-1,2-ethylenebis(4,7-dimethylindenyl)hafnium dimethyl was preactivated with trityl tetrakis(pentafluorophenyl)borate (obtained from Single-Site Catalysts, LLC). The rest of the catalysts were preactivated with N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate (obtained from Albemarle). For catalyst systems with preactivation, the catalysts were activated with cocatalyst at a molar ratio of 1:1 to 1:1.1 in 700 ml of toluene at least 10 minutes prior to the polymerization reaction. The catalyst systems were diluted to a concentration of catalyst ranging from 0.2 to 1.4 mg/ml in toluene. The catalyst solution was used for all polymerization runs carried out in the same day. New batch of catalyst solution was prepared in case that more than 700 ml of catalyst solution was consumed in

one day. Each catalyst solution was pumped through separate lines. Catalysts were mixed in a manifold, and then fed into the reactor through a single line. In methylalumoxane activated systems, 280 ml of methylalumoxane (MAO, 10 wt.% in toluene, from Albemarle) was diluted in 1000 ml of toluene, and the solution was stored in a 5-liter stainless cylinder. Catalysts were diluted to a concentration ranging from 0.2 to 1.4 mg/ml in toluene. Each catalyst solution and the methylalumoxane solution were pumped through separate lines. Catalysts and MAO were mixed in a manifold, and then fed into the reactor through a single line. The connecting tube between the catalyst manifold and reactor inlet was about 1 meter long.

[00318] All catalyst solutions were kept in an inert atmosphere with <1.5 ppm water content and fed into reactor by metering pumps. Catalyst and monomer contacts took place in the reactor. Catalyst pumps were calibrated periodically using toluene as the calibrating medium. Catalyst concentration in the feed was controlled through changing the catalyst concentration in catalyst solution and/or changing in the pumping rate of catalyst solution. The pumping rate of catalyst solution varied in a range of 0.2 to 5 ml/minute.

[00319] As an impurity scavenger, 55 ml of tri-iso-butyl aluminum (25wt.% in toluene, Akzo Noble) was diluted in 22.83 kilogram of hexane. The diluted tri-iso-butyl aluminum solution was stored in a 37.9-liter cylinder under nitrogen blanket. The solution was used for all polymerization runs until about 90% of consumption, then a new batch was prepared. Pumping rates of the tri-iso-butyl aluminum solution varies from polymerization reaction to reaction, ranging from 0 (no scavenger) to 4 ml per minutes.

[00320] For polymerization reactions involving alpha, omega-dienes, 1,9-decadiene was diluted to a concentration ranging from 4.8 to 9.5 vol.% in toluene. The diluted solution was then fed into reactor by a metering pump through a comonomer line. (The 1,9-decadiene was obtained from Aldrich and was purified

by first passing through alumina activated at high temperature under nitrogen, followed by molecular sieve activated at high temperature under nitrogen.)

[00321] The reactor was first cleaned by continuously pumping solvent (e.g., hexane) and scavenger through the reactor system for at least one hour at a maximum allowed temperature (about 150°C). After cleaning, the reactor was heated/cooled to the desired temperature using water/steam mixture flowing through the reactor jacket and controlled at a set pressure with controlled solvent flow. Monomers and catalyst solutions were then fed into the reactor when a steady state of operation was reached. An automatic temperature control system was used to control and maintain the reactor at a set temperature. Onset of polymerization activity was determined by observations of a viscous product and lower temperature of water-steam mixture. Once the activity was established and system reached equilibrium, the reactor was lined out by continuing operating the system under the established condition for a time period of at least five times of mean residence time prior to sample collection. The resulting mixture, containing mostly solvent, polymer and unreacted monomers, was collected in a collection box after the system reached a steady state operation. The collected samples were first air-dried in a hood to evaporate most of the solvent, and then dried in a vacuum oven at a temperature of about 90 °C for about 12 hours. The vacuum oven dried samples were weighed to obtain yields. All the reactions were carried out at a pressure of 2.41 MPa-g and in the temperature range of 45 to 130°C.

Examples 1-4

[00322] Four samples were made with rac-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl) (cyclododecylamido)titanium dimethyl at a temperature 115 °C over a range of catalyst ratios. The polymerization reactions followed the general procedure described above. The detailed experimental conditions and results are presented in Table 1.

Table 1				
Example	1	2	3	4
Catalyst #1	A	A	A	A
Catalyst #1 feed rate (mole/min)	4.83E-06	3.66E-06	3.00E-06	2.68E-06
Catalyst #2	B	B	B	B
Catalyst #2 feed rate (mole/min)	3.64E-07	3.64E-07	3.64E-07	3.64E-07
Propylene feed rate (g/min)	14	14	14	14
Hexane feed rate (ml/min)	90	90	90	90
Polymerization temp (°C)	115	115	115	115
Mn (kg/mol)	19.1	18.2	16.4	16.9
Mw (kg/mol)	31	28.3	25.7	26.7
Mz (kg/mol)	66.1	52.4	46.9	53.1
g' @ Mz	1.02	0.99	0.96	0.9
Tc (°C)	90.5	98.8	97.7	97.1
Tm (°C)	140.5	143.2	143.8	142.8
Tg (°C)	-17.7	-10.4	-10.4	-11.3
Heat of fusion (J/g)	21.7	25.7	34.7	35.1
Viscosity @190 °C (cps)	1540	1340	1240	798
Conversion (%)	95.3	89.6	87.1	92.8
Catalyst activity (kg polymer/ g catalyst)	5.7	6.9	8.0	9.4
Catalysts:				
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl				
B=rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl				

Examples 5-8

[00323] Four samples were made with rac-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl)(t-butylamido)titanium dimethyl at a temperature of 100 °C over a range of catalyst ratio. The polymerization reactions followed the general procedure described above. The detailed experimental conditions and results are presented in Table 2.

Table 2				
Example	5	6	7	8
Catalyst #1	F	F	F	F
Catalyst #1 feed rate (mole/min)	4.92E-06	4.92E-06	4.92E-06	4.92E-06
Catalyst #2	B	B	B	B
Catalyst #2 feed rate (mole/min)	5.67E-07	8.50E-07	1.13E-06	1.42E-06
Propylene feed rate (g/min)	14	14	14	14
Hexane feed rate (ml/min)	90	90	90	90
Polymerization temperature (°C)	100	100	100	100
Mn (kg/mol)	12.1	11.9	8.8	12.4
Mw (kg/mol)	29.4	30.7	26.3	28
Mz (kg/mol)	84.3	81.6	80.7	84.7
g' @ Mz	0.93	0.88	0.87	0.84
Tc (°C)	95.8	98.4	96.1	95.8
Tm (°C)	145.2	145.7	143.3	143.0
Tg (°C)	-9.6	-10.4	-11.1	-10.0
Heat of fusion (J/g)	21.4	32.4	30.0	33.0
Viscosity @190 °C (cps)	1100	1040	840	675
Conversion (%)	88.63	91.73	68.09	77.23
Catalyst activity (kg polymer/ g catalyst)	6.38	6.08	4.18	4.42
Catalysts:				
B = rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl				
F= dimethylsilyl(tetramethylcyclopentadienyl)(tert-butylamido) titanium dimethyl				

Examples 9-15

[00324] Seven samples were made with dimethylsilylbis(indenyl)hafnium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl at a catalyst ratio of about 80.0 molar percent over a range of temperatures. The polymerization reactions followed the general procedure described above. The detailed experimental conditions and results are presented in Table 3. The data show that temperature has appreciable effects on crystallinity, Mw, Mw/Mn, and level of branching. The population can also be manipulated through reaction temperatures since the reaction kinetics of each catalyst has unique response to

polymerization temperatures.

Table 3							
Example	9	10	11	12	13	14	15
Catalyst #1	A	A	A	A	A	A	A
Catalyst #1 feed rate (mole/min)	5.22E-06	5.22E-06	5.22E-06	5.22E-06	5.22E-06	5.22E-06	5.22E-06
Catalyst #2	C	C	C	C	C	C	C
Catalyst #2 feed rate (mole/min)	1.31E-06	1.31E-06	1.31E-06	1.31E-06	1.31E-06	1.31E-06	1.31E-06
Propylene feed rate (g/min)	14	14	14	14	14	14	14
Hexane feed rate (ml/min)	90	90	90	90	90	90	90
Polymerization temperature (°C)	110	105	100	95	90	85	80
Mn (kg/mol)	8.5	8.2	9.8	11.1	22.5	26.6	30.9
Mw (kg/mol)	15.7	17.1	19.8	23.5	41.1	46.9	55.8
Mz (kg/mol)	30.6	37.9	42.2	40.4	79.8	84.8	95.5
g' @Mz	1	0.97	0.95	0.97	0.98	0.97	0.98
Tc (°C)	22.8	31.6	40.5	47.8	53.5	61.0	64.8
Tm (°C)	74.7	82.3	87.4	94.3	103.3	107.7	113.7
Tg (°C)	-15.5	-13.0	-12.0	-10.0	-7.5	-7.5	-6.0
Heat of fusion (J/g)	14.4	16.6	21.5	26.0	21.0	27.8	26.7
Viscosity @190 °C (cps)	227	272	441	813	5280	7250	15400
Catalysts:							
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl							
C=rac-dimethylsilyl bis (indenyl) hafnium dimethyl							

Examples 16-19

[00325] Four samples were made with rac-dimethylsilylbis(indenyl)hafnium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl at a temperature of 100°C and various catalyst ratios. The polymerization reactions followed the general procedure described above. The detailed experimental conditions and results are presented in Table 4. The data show that catalyst ratios have appreciable effects on crystallinity, Mw, Mw/Mn, and level of branching. The population can also be manipulated through reaction temperatures since the reaction kinetics of each catalyst has unique response to polymerization

temperatures.

Table 4				
Example	16	17	18	19
Catalyst #1	A	A	A	A
Catalyst #1 feed rate (mole/min)	8.49E-07	8.49E-07	8.49E-07	8.49E-07
Catalyst #2	C	C	C	C
Catalyst #2 feed rate (mole/min)	5.51E-07	8.26E-07	1.28E-06	1.93E-06
Propylene feed rate (g/min)	14	14	14	14
Hexane feed rate (ml/min)	90	90	90	90
Polymerization temperature (°C)	100	100	100	100
Mn (kg/mol)	17.1	14.1	9.6	7.3
Mw (kg/mol)	28	20.7	14.3	10.6
Mz (kg/mol)	65	37.6	24.9	18.2
g' @ Mz	1.05	0.97	0.92	0.94
Tc (°C)	61.2	55.2	30.8	28.8
Tm (°C)	107.3	97.6	76.9	64.3
Tg (°C)	-8.9	-14.5	-15.3	-14.6
Heat of fusion (J/g)	29.9	31.2	19.9	7.6
Viscosity @ 190 °C (cps)	1355	412	165	87
Conversion (%)	86.20	91.89	100.56	97.90
Catalyst activity (kg polymer/g catalyst)	18.74	16.49	13.97	10.34
Catalysts:				
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl				
C = rac-dimethylsilyl bis (indenyl) hafnium dimethyl				

Examples 20-34

[00326] Fifteen samples were made with rac-dimethylsilylbis(2-methyl-4-phenylindenyl) zirconium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl catalysts, following the general procedure described above with the exception that a small quantity of 1,9-decadiene was fed as the diolefin monomer

along with propylene as the alpha-olefin monomer. The detailed experimental conditions and results are presented in Tables 5 and 6.

Table 5					
Example	20	21	22	23	24
Catalyst #1	A	A	A	A	A
Catalyst #1 feed rate (mole/min)	6.53E-06	6.53E-06	6.53E-06	6.53E-06	6.53E-06
Catalyst #2	B	B	B	B	B
Catalyst #2 feed rate (mole/min)	6.92E-07	3.64E-07	3.64E-07	2.19E-07	2.19E-07
Propylene feed rate (g/min)	14	14	14	8.3	10
1,9 decadiene feed rate (ml/min)	0.19	0.19	0.19	0.13	0.13
Hexane feed rate (ml/min)	90	90	90	90	90
Polymerization temperature (°C)	120	125	120	120	110
Mn (kg/mol)	15.6	14.7	14.3	---	---
Mw (kg/mol)	23	24.6	29.5	---	---
Mz (kg/mol)	55.2	64.2	85	---	---
g' @Mz	0.85	0.91	0.85	---	---
Tc (°C)	86.5	91.8	91.8	86.5	87.6
Tm (°C)	116.6	128.7	129.7	128.8	137.6
Tg (°C)	-10.6	-11.1	-9.7	-9.4	-7.5
Heat of fusion (J/g)	31.8	32.1	26.0	17.0	19.4
Viscosity @ 190 °C (cps)	721	725	1240	448	2240
Conversion (%)	93.32	77.57	81.12	77.49	85.13
Catalyst activity (kg polymer/ g catalyst)	4.00	3.54	3.70	2.15	2.85
Catalysts:					
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl					
B = rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl					

Table 5 (continued)

Example	25	26	27	28	29
Catalyst #1	A	A	A	A	A
Catalyst #1 feed rate (mole/min)	5.22E-06	5.22E-06	5.22E-06	6.53E-06	6.53E-06
Catalyst #2	B	B	B	B	B
Catalyst #2 feed rate (mole/min)	7.65E-07	7.65E-07	7.65E-07	2.19E-07	4.74E-07
Propylene feed rate (g/min)	14	14	14	10	14
1,9 decadiene feed rate (ml/min)	0.24	2.24	0.19	0.13	0.19
Hexane feed rate (ml/min)	90	90	90	90	90
Polymerization temperature (°C)	115	117	110	125	115
Mn (kg/mol)	20		23		17.3
Mw (kg/mol)	36.7		45.5		34.5
Mz (kg/mol)	111.9		104		97.1
g' @Mz	0.68		0.75		0.75
Tc (°C)	91.1	87.0	96.8	77.3	88.5
Tm (°C)	136.6	133.7	134.2	130.0	136.3
Tg (°C)	-9.6	-10.7	-9.7	-11.2	-12.4
Heat of fusion (J/g)	51.5	39.5	42.5	15.1	35.8
Viscosity @ 190 °C (cps)	880	518	1850	661	1040
Conversion (%)	92.20	89.30	96.84	80.62	91.15
Catalyst activity (kg polymer/ g catalyst)	4.72	4.57	4.96	2.70	4.07
Catalysts:					
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl					
B = rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl					

Table 6

Example	30	31	32	33	34
Catalyst #1	A	A	A	A	A
Catalyst #1 feed rate (mole/min)	1.02E-06	5.22E-06	6.53E-06	6.53E-06	6.53E-06
Catalyst #2	B	B	B	B	B
Catalyst #2 feed rate (mole/min)	1.13E-07	7.65E-07	4.74E-07	6.20E-07	3.64E-07
Propylene feed rate (g/min)	14	14	14	14	14
1,9 decadiene feed rate (ml/min)	0.19	0.24	0.19	0.19	0.19
Hexane feed rate (ml/min)	90	90	90	90	90
Polymerization temperature (°C)	115	115	110	110	115
Mn (kg/mol)	20.3	14.9	13.6	16.1	17.6
Mw (kg/mol)	96.2	34.3	30.2	30.4	36.5
Mz (kg/mol)	636.2	114.8	67.6	68.7	91.5
g' @Mz	0.46	0.72	0.95	0.88	0.85
Tc (°C)		91.4	91.8	94.3	84.4
Tm (°C)		129.3	140.5	140.6	137.2
Tg (°C)		-10.0	-11.2	-8.9	-8.2
Heat of fusion (J/g)		46.9	28.3	38.4	20.8
Viscosity @ 190 °C (cps)		1030	1870	1360	2470
Conversion (%)	56.38	95.32	97.29	97.24	87.82
Catalyst activity (kg polymer/ g catalyst)	15.44	4.88	4.34	4.23	4.00
Catalysts:					
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl					
B = rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl					

Examples 35-39

[00327] Five samples were made with dimethylsilylbis (indenyl) hafnium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl at a catalyst ratio of 75 mol.% and over a range of temperatures from 85 to 105°C, following the general procedure described above with the exception that a small quantity of 1,9-decadiene was fed as the diolefin monomer along with propylene

as the alpha-olefin monomer. The detailed experimental conditions and results are presented in Table 7.

Table 7					
Example	35	36	37	38	39
Catalyst #1	A	A	A	A	A
Catalyst #1 feed rate (mole/min)	5.22E-06	5.22E-06	5.22E-06	5.22E-06	5.22E-06
Catalyst #2	C	C	C	C	C
Catalyst #2 feed rate (mole/min)	1.75E-06	1.75E-06	1.75E-06	1.75E-06	1.75E-06
Propylene feed rate (g/min)	14	14	14	14	14
1,9 decadiene feed rate (ml/min)	0.24	0.24	0.24	0.24	0.24
Hexane feed rate (ml/min)	90	90	90	90	90
Polymerization temperature (°C)	105	100	95	90	85
Mn (kg/mol)	9.6	15.7	14.1	15.2	29.3
Mw (kg/mol)	16.5	24.6	30	40.4	69.1
Mz (kg/mol)	33.4	48.4	70.7	103.1	222.6
g' @ Mz	0.89	0.81	0.8	0.76	0.66
Tc (°C)	25.2	29.4	30.9	41.8	53.5
Tm (°C)	67.3	76.1	81.2	91.3	102.3
Tg (°C)	-15.4	-13.3	-13.1	-8.1	-7.4
Heat of fusion (J/g)	13.4	19.5	20.9	25.7	33.3
Viscosity @ 190 °C (cps)	194	291	568	1650	5210
Catalysts:					
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl					
C = rac-dimethylsilyl bis (indenyl) hafnium dimethyl					

Examples 40-43

[00328] Four samples were made with rac-dimethylsilylbis(indenyl)hafnium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl, following the general procedure described above with the exception that a small quantity of 1,9-decadiene was fed as the diolefin monomer along with propylene as the alpha-olefin monomer. The detailed experimental conditions and results are presented in Table 8.

Table 8				
Example	40	41	42	43
Catalyst #1	A	A	A	A
Catalyst #1 feed rate (mole/min)	8.49E-07	8.49E-07	8.49E-07	5.22E-06
Catalyst #2	C	C	C	C
Catalyst #2 feed rate (mole/min)	8.26E-07	5.51E-07	5.51E-07	5.82E-07
Propylene feed rate (g/min)	14	14	14	14
1,9 decadiene feed rate (ml/min)	0.05	0.02	0.05	0.19
Hexane feed rate (ml/min)	90	90	86	90
Polymerization temperature (°C)	100	95	90	95
Mn (kg/mol)	10.5	16.1	23	28.3
Mw (kg/mol)	19.5	24.4	39.4	94.8
Mz (kg/mol)	38	44.3	71.3	455.2
g' @Mz	0.92	0.93	0.93	0.54
Tc (°C)	47.7	53.7	71.0	37.4
Tm (°C)	94.4	98.6	112.5	101.2
Tg (°C)	-12.3	-11.1	-24.6	-10.3
Heat of fusion (J/g)	30.8	31.6	44.6	22.4
Viscosity @ 190 °C (cps)	327	625	2370	---
Conversion (%)	93.80	---	98.62	---
Catalyst activity (kg polymer/ g catalyst)	16.83	---	21.44	---
Catalysts:				
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl				
C = rac-dimethylsilyl bis (indenyl) hafnium dimethyl				

Examples 44-47

[00329] Four samples were made using rac-1,2-ethylene-bis(4,7-dimethylindenyl)hafnium dimethyl and dimethylsilyl-(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl at a temperature 110°C over a range of catalyst ratios. The conditions used for examples 44 to 47, which included diolefin incorporation, followed the general procedure described above with the exception that a small quantity of 1,9-decadiene was fed as the diolefin monomer along with propylene as the alpha-

olefin monomer. The detailed experimental conditions and results are presented in Table 9.

Table 9				
Example	44	45	46	47
Catalyst #1	A	A	A	A
Catalyst #1 feed rate (mole/min)	6.53E-06	3.79E-06	2.74E-06	2.09E-06
Catalyst #2	D	D	D	D
Catalyst #2 feed rate (mole/min)	4.25E-07	4.25E-07	4.25E-07	4.25E-07
Propylene feed rate (g/min)	14	14	14	14
1,9 decadiene feed rate (ml/min)	0.09	0.09	0.09	0.09
Hexane feed rate (ml/min)	90	90	90	90
Polymerization temperature (°C)	115	115	115	115
Mn (kg/mol)	21.5	20	21.2	16.1
Mw (kg/mol)	36.2	32.7	34	33.5
Mz (kg/mol)	100.1	95.6	123.7	128.8
Tc (°C)	41.0	51.5	59.8	74.4
Tm (°C)	94.3	97.6	103.4	109.4
Tg (°C)	-22.8	-23.8	-12.5	-18.9
Heat of fusion (J/g)	4.1	6.8	11.3	15.8
Viscosity @ 190 °C (cps)	2090	1750	1570	1230
Conversion (%)	83.58	83.95	71.84	63.10
Catalyst activity (kg polymer/ g catalyst)	3.80	6.26	7.08	7.78
Catalysts:				
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl				
D=rac-1,2-ethylene bis (4,7-dimethylindenyl)hafnium dimethyl				

Examples 48-51

[00330] Four samples were made with rac-dimethylsilylbis(2-methylindenyl)zirconium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl at a temperature of 80°C and over a range of catalyst ratios from 74 to 84 mol.%, following the general procedure described above with the exception that a small quantity of 1,9-decadiene was fed as the diolefin monomer along with propylene as the alpha-olefin monomer. The detailed experimental conditions and results are presented in Table 10.

Table 10				
Example	48	49	50	51
Catalyst #1	A	A	A	A
Catalyst #1 feed rate (mole/min)	6.53E-06	6.53E-06	6.53E-06	6.53E-06
Catalyst #2	E	E	E	E
Catalyst #2 feed rate (mole/min)	1.23E-06	1.57E-06	1.92E-06	2.26E-06
Propylene feed rate (g/min)	14	14	14	14
1,9 decadiene feed rate (ml/min)	0.14	0.14	0.14	0.14
Hexane rate (ml/min)	90	90	90	90
Polymerization temperature (°C)	80	80	80	80
Mn (kg/mol)	19.9	16	11.4	10
Mw (kg/mol)	43.8	36.9	25.9	19.2
Mz (kg/mol)	106.3	72.3	54.5	38.8
g' @ Mz	0.88	0.93	0.93	0.93
Tc (°C)	49.0	53.3	58.6	53.1
Tm (°C)	109.9	107.8	103.2	102.0
Tg (°C)	-10.7	-7.4	-9.1	-9.6
Heat of fusion (J/g)	25.8	29.4	31.4	37.7
Viscosity @ 190 °C (cps)	4680	2040	952	464
Catalysts:				
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl				
E=rac-dimethylsilyl bis(2-methylindenyl)zirconium dimethyl				

Examples 52-57

[00331] Six samples were made with rac-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dimethyl and dimethylsilyl-(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl at a temperature range of 80 to 95°C and a catalyst ratio of about 87 molar percent, following the general procedure described above with the exception that (1) a small quantity of 1,9-decadiene was fed as the diolefin monomer along with propylene as the alpha-olefin monomer; (2) A small amount of hydrogen was also fed in the reactor. The detailed experimental conditions and results are presented in Table 11. Examples 52-57 show that addition of hydrogen can effectively manipulate Mw, Mw/Mn, crystallinity, the ratio of crystalline phase to the

amorphous phase, in addition to the control obtained through catalyst selections and process conditions such as temperatures.

Table 11

Table 11						
Example	52	53	54	55	56	57
Catalyst #1	A	A	A	A	A	A
Catalyst #1 feed rate (mole/min)	6.10E-06	6.10E-06	6.10E-06	6.10E-06	6.10E-06	6.10E-06
Catalyst #2	B	B	B	B	B	B
Catalyst #2 feed rate (mole/min)	2.83E-07	2.83E-07	2.83E-07	2.83E-07	1.98E-07	1.98E-07
Propylene (g/min)	14	14	14	14	14	14
1, 9 decadiene feed rate (ml/min)	0.19	0.19	0.19	0.19	0.19	0.19
H2 feed rate (cc/min)	50	50	50	50	70	70
Hexane feed rate (ml/min)	90	90	90	90	90	90
Polymerization temperature (°C)	95	90	85	80	90	80
Mn (kg/mol)	12.6	11	12.5	15.7	18.1	11.7
Mw (kg/mol)	27.5	43.2	42.3	85.3	34	29.8
Mz (kg/mol)	72.2	127	153.4	468.3	126	99
g' @ Mz	0.82	0.74	0.8	0.66	0.8	0.84
Tc (°C)	95.7	95.8	97.4	97.0	98.9	97.7
Tm (°C)	141.0	145.1	145.8	147.0	144.5	145.1
Tg (°C)	-14.6	-13.3	-12.3	-9.8	-17.2	-14.8
Heat of fusion (J/g)	38.5	45.4	35.9	35.4	49.3	39.2
Viscosity @ 190 °C (cps)	668	1049	2148	16090	810	822
Catalysts:						
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl						
B = rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl						

Examples 58-60

[00332] Three samples were made with rac-dimethylsilylbis (2-methyl-4-phenylindenyl) zirconium dimethyl and dimethylsilyl-(tetramethylcyclopentadienyl)(cyclododecylamido) titanium dimethyl at a temperature 115°C and a catalyst ratio of about 87 molar percent, following the general procedure described above with the following exceptions: (1) a small

quantity of 1,9-decadiene was fed as the diolefin monomer; (2) both rac-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl catalysts were premixed and diluted in toluene, then fed into catalyst manifold without preactivation; (3) N, N-dimethylanilinium tetrakis(pentafluorophenyl) borate was diluted in toluene and then fed into catalyst manifold; (4) catalyst activation started in catalyst manifold. The detailed experimental conditions and results are presented in Table 12. Examples 58-60 demonstrate that catalysts can be activated in-line just prior to the reactor and in reactor.

Table 12

Example	58	59	60
Catalyst #1	A	A	A
Catalyst #1 feed rate (mole/min)	4.06E-06	2.54E-06	1.52E-06
Catalyst #2	B	B	B
Catalyst #2 feed rate (mole/min)	2.95E-07	1.84E-07	1.11E-07
Propylene (g/min)	14	14	14
1, 9 decadiene feed rate (ml/min)	0.14	0.14	0.14
Hexane feed rate (ml/min)	90	90	90
Polymerization temperature (°C)	115	115	115
Mn (kg/mol)	13.2	18.2	24.2
Mw (kg/mol)	34.5	50.8	69.9
Mz (kg/mol)	99.6	169	248.6
g' @ Mz	0.79	0.72	0.69
Tc (°C)	90.6	92.9	93.0
Tm (°C)	137.0	139.6	142.6
Tg (°C)	-10.8	-10.0	-8.7
Heat of fusion (J/g)	32.5	32.9	28.4
Viscosity @190 °C (cps)	1657	3170	11600
Conversion (%)	89.64	77.50	95.59
Catalyst activity (kg polymer/ g catalyst)	6.43	8.90	18.29
Catalysts:			
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl			
B = rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl			

Examples 61-66

[00333] Six samples were made with dimethylsilylbis (2-methyl-4-phenylindenyl) zirconium dimethyl and dimethylsilyl(tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl at a temperature range of 105 to 130 °C and a catalyst ratio of about 84.6 molar percent, following the general procedure described above with the following exceptions: (1) a small quantity of 1,9-decadiene was fed as the diolefin monomer; (2) ethylene was added to the reactor. The detailed experimental conditions and results are presented in Table 13. Ethylene content in the polymer was obtained from by Fourier Transformation Infrared analysis (FTIR).

Table 13						
Example	61	62	63	64	65	66
Catalyst #1	A	A	A	A	A	A
Catalyst #1 feed rate (mole/min)	1.02E-06	1.02E-06	1.02E-06	1.02E-06	1.02E-06	1.02E-06
Catalyst #2	B	B	B	B	B	B
Catalyst #2 feed rate (mole/min)	1.84E-07	1.84E-07	1.84E-07	1.84E-07	1.84E-07	1.84E-07
Propylene feed rate (g/min)	20	20	20	20	20	20
1, 9 decadiene feed rate (ml/min)	0.186	0.186	0.186	0.186	0.186	0.186
Ethylene feed rate (SLPM)	0.2	0.2	0.2	0.2	0.2	0.2
Hexane feed rate (ml/min)	90	90	90	90	90	90
Polymerization temperature (°C)	130	125	120	115	110	105
Mn (kg/mol)	13.1	12.3	11.8	15.1	15.3	17.7
Mw (kg/mol)	37.3	36.2	40.5	47.7	45.2	53.8
Mz (kg/mol)	149.2	122	132.1	153.9	206.8	180.7
g' @ Mz	0.67	0.65	0.63	0.61	0.56	0.56
Tc (°C)	80.4	79.6	84.6	85.5	87.7	86.6
Tm (°C)	121.8	121.9	124.6	125.2	126.1	126.2
Tg (°C)	-15.0	-15.2	-14.9	-14.8	-15.0	-15.6
Heat of fusion (J/g)	32.4	43.3	51.7	50.5	50.4	49.7
Viscosity @190 °C (cps)	1440	977	1090	1510	1530	1720
Ethylene content from	4.3	3.5	3	2.6	2.9	2.9

FTIR (wt. %)						
Conversion (%)	68.11	82.57	89.87		92.79	92.18
Catalyst activity (kg polymer/ g catalyst)	24.92	30.21	32.88		33.95	33.73
Catalysts:						
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl						
B = rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl						

Examples 67-71

[00334] All these samples were made with dimethylsilylbis (2-methyl-4-phenylindenyl) zirconium dimethyl and dimethylsilyl-(tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl at a temperature range of 105 to 115 °C except example 69, following the general procedure described above with the following exceptions: (1) a small quantity of dicyclopentadiene was used in example 67 (The dicyclopentadiene, obtained from aldrich, was first dissolved in toluene. The solution was then purified by passing through alumina activated at high temperature under nitrogen, followed by molecular sieve activated at high temperature under nitrogen.); (2) 1-butene was used in examples 68 and 70; (3) 1,9-decadiene and 1-hexene were fed as the diolefin monomer and comonomer, respectively in example 71. Example 69 was made using dimethylsilyl-(tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl and rac-dimethylsilyl bis(2-methylindenyl)zirconium dimethyl catalysts. The detailed experimental conditions and results are presented in Table 14.

Table 14					
Example	67	68	69	70	71
Catalyst #1	A	A	A	A	A
Catalyst #1 feed rate (mole/min)	5.22E-06	5.22E-06	2.09E-06	5.22E-06	5.22E-06
Catalyst #2	B	B	E	B	B
Catalyst #2 feed rate (mole/min)	7.65E-07	7.65E-07	4.25E-07	7.65E-07	7.65E-07
Propylene feed rate (g/min)	14	14	14	14	14
Comonomer	dicyclopentadiene	Butene-1	---	Butene-1	1,9 decadiene
Comonomer feed rate (ml/min)	0.23	0.6	---	2.5	0.206
1-hexene flow rate (ml/min)	---	---	---	---	3.29
Hexane feed rate (ml/min)	90	90	90	90	90
Polymerization temperature (°C)	110	115	110	105	115
Mn (kg/mol)	---	---	12.2	---	---
Mw (kg/mol)	---	---	30.6	---	---
Mz (kg/mol)	---	---	84.3	---	---
Tc (°C)	---	---	72.3	86.0	42.6
Tm (°C)	---	---	112.1	124.8	89.8
Tg (°C)	---	---	-22.4	-12.3	-15.2
Heat of fusion (J/g)	---	---	23.3	38.4	27.0
Viscosity @190 °C (cp)	665	563	1420	1100	524
Conversion (%)	74.40	98.07	65.78	---	98.98
Catalyst activity (kg polymer/ g catalyst)	3.81	5.15	8.11	---	5.77
Catalysts					
A=dimethylsilyl (tetramethylcyclopentadienyl) (cyclododecylamido) titanium dimethyl					
B = rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium dimethyl					

Example 72

[00335] Example 72 was carried out in a 500-ml autoclave batch reactor. 125 ml of purified toluene was first added into the stainless steel autoclave reactor, followed by addition of 0.1 ml of tri-iso-butyl aluminum (TIBAL) solution (25-wt.% of TIBAL diluted in 5 ml of toluene). The mixture was then stirred and